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INDENYL- AND FLUORENYL-TRANSITION METAL COMPLEXES

XII *. SYNTHESIS AND DEPROTONATION OF η^6-FLUORENE-MOLYBDENUM AND -TUNGSTEN TRICARBONYLS AND η^6-INDENEMOLYBDENUM TRICARBONYL **

L.N. NOVIKOVA, N.A. USTYNYUK *, V.E. ZVORYKIN,

A.N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences, 117813, Moscow, Vavilova St., 28 (U.S.S.R.)

L.S. DNEPROVSKAYA and Yu.A. USTYNYUK

M.V. Lomonosov Moscow State University, Department of Chemistry, 117234, Moscow, Leninskie Gory (U.S.S.R.)

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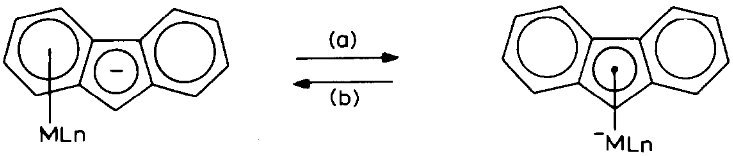
Summary

$Py_3Mo(CO)_3$ reacts with fluorene and indene in ether in the presence of $(C_2H_5)_2O \cdot BF_3$ to give η^6-$C_{13}H_{10}Mo(CO)_3$ (I) and η^6-$C_9H_8Mo(CO)_3$ (III), respectively. The analogous reactions of $Py_3W(CO)_3$ lead to η^6-$C_{13}H_{10}W(CO)_3$ (II) and η^5-$C_9H_7(CO)_3WH$ (V), respectively. On deprotonation of I–III the corresponding unstable η^6-anions are formed which rearrange into η^5-isomers.

The rate of these rearrangements is considerably higher than that of the analogous process for η^6-$C_{13}H_9Cr(CO)_3^-$.

Introduction

In the course of our systematic study of indenyl and fluorenyl Group VIA metal derivatives we have found a new type of metallotropic tautomerism [1,2] consisting of reversible migrations of the $Cr(CO)_3$ group between the five- and six-membered rings in fluorenylchromium tricarbonyl anions (eq. 1).



(1)

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[*] For part XI see ref. 10.

[**] Dedicated to Prof. Oleg A. Reutov on the occasion of his 65th birthday.

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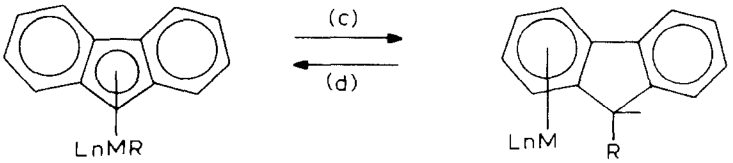


(2)

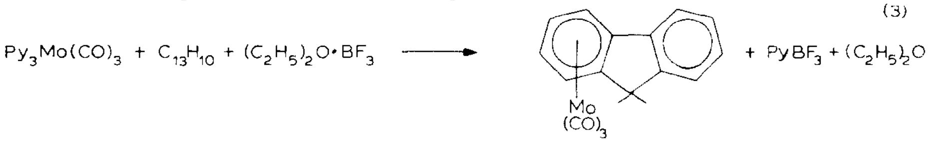
The search for reversible rearrangements, shown by eq. 2, is also of interest. We have found [3] "ricochet" isomerizations of η^5-($C_{13}H_9$ and C_9H_7)(CO)$_3$CrR derivatives (process (c)), but up to now we have not been able to find the reverse transformations (d). Thus, we studied both (a) $\rightleftarrows$ (b) and (c) processes for chromium derivatives (MLn = Cr(CO)$_3$). For a better understanding of these reactions it seemed important to carry out an investigation of the corresponding molybdenum and tungsten derivatives. In this paper we report on the synthesis of the previously unknown complexes η^6-$C_{13}H_{10}M(CO)_3$ (I, M = Mo; II, M = W) and η^6-$C_9H_8Mo(CO)_3$ (III) and also their deprotonation.

Results and discussion

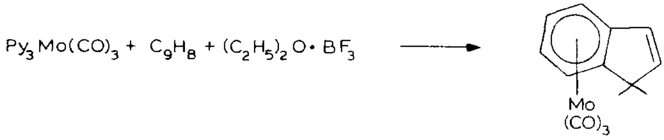
The thermal reaction of fluorene with $Mo(CO)_6$ in diglyme/heptane mixture at 140°C does not give I; the tungsten compound II is formed under the conditions in a yield of about 1%. In the reactions of indene with $M(CO)_6$, compounds with an η^5-structure are formed [4,5].

We have synthesized I–III by treating $Py_3M(CO)_3$ (M = Mo, W) with arene in ether in the presence of boron trifluoride etherate. This method was suggested by Öfele [6] for the preparation of arenechromium tricarbonyls and was spread by Nesmeyanov and co-workers [7] for arenemolybdenum tricarbonyls. In the case of molybdenum compounds I and III the reaction proceeds in ether at room temperature and is completed in 30–45 min (eq. 3, 4).

(3)



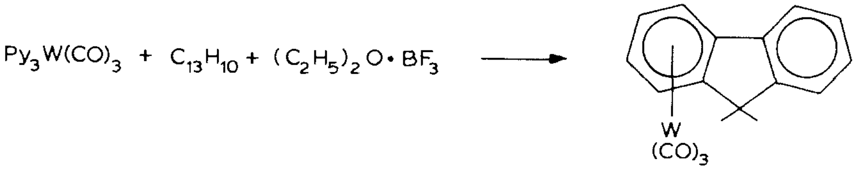
(I, 12%)



(4)

(III, 18%)

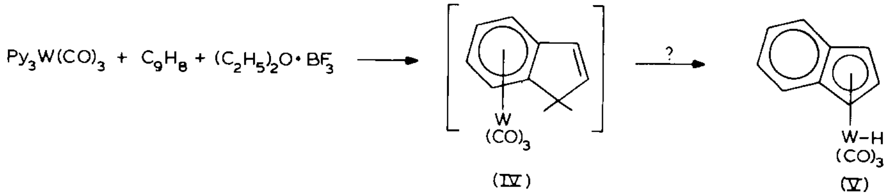
Under these conditions the reactivity of $Py_3W(CO)_3$ is too low and in order to prepare II we conducted reaction 5 in dibutyl ether at 60–65°C (eq. 5).



(5)

(II, 33%)

When $Py_3W(CO)_3$ was treated with indene under the same conditions, η^5-$C_9H_7(CO)_3WH$ (V) rather than η^6-$C_9H_8W(CO)_3$ (IV) was formed. It was previously prepared by us on protonation of η^5-$C_9H_7(CO)_3W^-$ [8].



(6)

It is interesting to ascertain the way in which V is formed. If the η^6-complex IV is an intermediate which is converted further into V, then this is the first example of a "retro-ricochet" rearrangement consisting of the migration of hydrogen from position 1 to the metal and tungsten shift to the five-membered ring (process (d), eq. 2). On the whole, the reactions of $Py_3Mo(CO)_3$ and $Py_3W(CO)_3$ with indene should proceed in the same way. Therefore the outcome of reaction 4 seems to indicate at first sight the above-mentioned pathway of reaction 6. Indirect justification of this tentative conclusion is the formation of (1,1-dimethylindene)tungsten tricarbonyl in the reaction of 1,1-dimethylindene with $Py_3W(CO)_3$ under the conditions of reaction 6.

On the other hand, process 6 can proceed directly on the five-membered ring without involving the six-membered ring, since, as shown by a special experiment, cyclopentadiene reacts with $Py_3W(CO)_3$ under the conditions of reaction 6. Unequivocal elucidation of the scheme of reaction 6 requires further study, which is currently under way.

The arenemolybdenum tricarbonyls I and III are yellow, crystalline substances, which decompose when kept under an argon atmosphere at room temperature for a few days. They are very sensitive to ethereal solvents and decompose instantaneously on dissolution in THF, glyme, diglyme and also in dimethylformamide, but they can be dissolved in ether and benzene without rapid decomposition. The stability of tungsten compound II is somewhat higher; it does not decompose as fast on dissolution in THF. All the complexes, I–III, were characterized by elemental analysis, IR, ^{1}H NMR and mass spectra.

The study of the deprotonation of I–III and rearrangements of the η^6-anions Ia–IIIa to the corresponding η^5-isomers Ib–IIIb is complicated by the fact that the stability of Ia–IIIa and of Ib and IIb is considerably lower than that of the starting neutral compounds. The choice of the deprotonating base also presents problems.

Since the molybdenum complexes I and III cannot exist in THF and other solvents of good coordinating ability, their deprotonation was accomplished in ether with the addition of a hexane solution of BuLi at −70°C. The formation of η^6-anions was accompanied by the deepening colour of the solution and deposition of a red precipitate. When the temperature was increased gradually to ~ −15°C, the precipitate dissolved and new bands appeared in the IR spectrum which can be assigned to the Li salts of the η^5-anions Ib (1732, 1788 and 1922 cm^{-1}) and IIIb (1738, 1790 and 1920 cm^{-1}) *. The intensities of these bands decrease rapidly when

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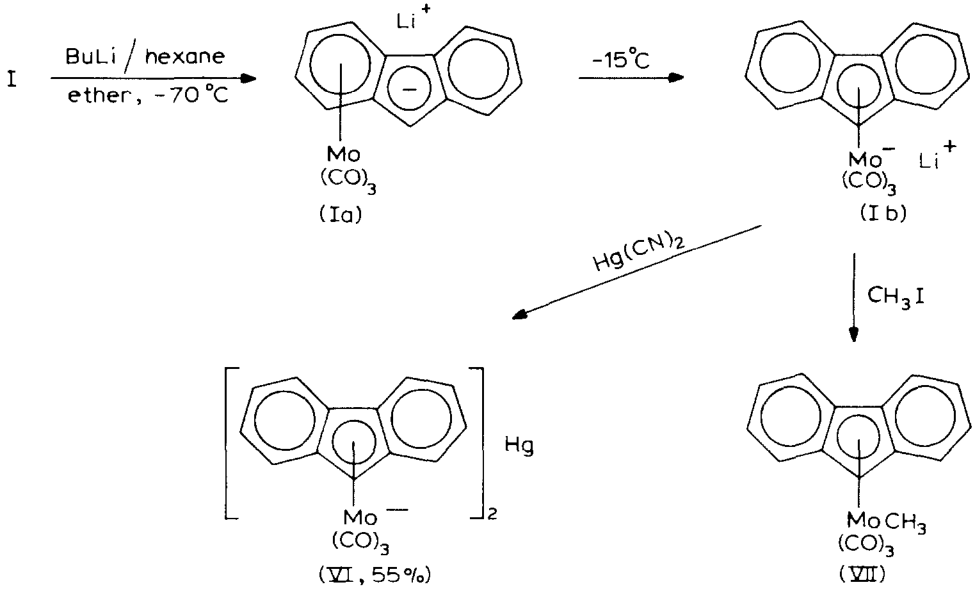
* Bands which could be assigned to the η^6-anions Ia and IIIa were not observed at either −15°C or at lower temperatures.

the solution is kept even below 0°C. On treatment of the reaction mixtures at −15°C with mercury cyanide and methyl iodide, the corresponding mercury and methyl derivatives were formed. These processes are shown in Scheme 1 for fluorenemolybdenum tricarbonyl (I).

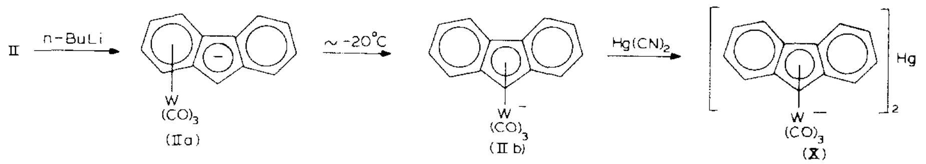


SCHEME 1

The mercury derivative VI was isolated and characterized by IR and NMR spectra; the formation of the σ-methyl derivative VII was established only with the IR spectrum: ν(CO) (ether) 1946, 2024 cm^{-1}. The analogously prepared complexes from IIIb $[\eta^5\text{-}C_9H_7(CO)_3Mo]_2Hg$ and $\eta^5\text{-}C_9H_7(CO)_3MoCH_3$) have been reported previously [5,8].

The tungsten anions IIa and IIb, like the neutral complex II, appear to be considerably more stable than their molybdenum analogues. In any case, II could be deprotonated by t-BuOM (M = K, Cs) in THF at −70°C and IR bands corresponding to IIa (Cs salt) could be observed.

The conversion IIa → IIb proceeds very quickly even at ~ −20 to −25°C, both anions being very unstable in THF and decomposing fast under these conditions. The somewhat greater stability of II and its anions in ether enables the processes shown in Scheme 2 to be accomplished in this solvent.



SCHEME 2

Since t-BuOK does not deprotonate II in ether, n-BuLi was used as the deprotonating agent. However, IIa and IIb were not observed in the IR spectrum because of their low solubility in ether below 0°C. Nevertheless, the mercury derivative X was isolated in a 33% yield.

The instability of the η^6- and η^5-fluorenyltungsten tricarbonyl anions necessitates the use of a special low-temperature technique for their detailed examination. Nonetheless, it can be concluded that the $\eta^6 \rightarrow \eta^5$ rearrangement for these anions proceeds considerably faster (and consequently the activation barrier is lower) than in the case of isostructural fluorenylchromium tricarbonyl anions [2].

Experimental

All operations were carried out in an argon atmosphere. THF and dibutyl ether were purified by refluxing over K/Na alloy and Na respectively, ether was purified over sodium ketyl benzophenone. All solvents were distilled prior to use. Silica gel L 40/100 μ (Chemapol, ČSSR) was used for column chromatography. $Py_3M(CO)_3$ (M = Mo, W) was prepared according to [9]. NMR spectra were run on a Varian XL 100 instrument, using tetramethylsilane as the internal standard.

Preparation of fluorenemolybdenum tricarbonyl (I)

To 1.0 g (6 mmol) of fluorene and 2.5 g (6 mmol) of $Py_3Mo(CO)_3$ in 100 ml of ether, 2.5 ml (18 mmol) of $Et_2O \cdot BF_3$ was added at room temperature and the mixture was stirred for 30–45 min. Then hexane (30 ml) was added, the solution was filtered through paper, and the filtrate was washed with water and dried over $MgSO_4$. Ether was removed by concentration of the mixture in vacuo; the remaining hexane solution was cooled over dry ice. The resulting yellow crystals were reprecipitated twice from benzene/heptane. Yield of I 0.25 g (12%). M.p. 159–161°C (dec.). $\nu(CO)(CH_2Cl_2)$ 1890, 1960 cm^{-1}. ^1H NMR (unless stated otherwise: δ (C_6D_6) ppm): AB subspectrum $(H(9)_{exo} + H(9)_{endo})$ δ_A 3.05 $(H(9)_{exo})$ δ_B 3.40 $(H(9)_{endo})$, J_{AB} 22 Hz; coordinated six-membered ring 4.78 (H(2) + H(3), 2H), 5.24(H(1), 1H), 5.56 (H(4), 1H); non-coordinated six-membered ring: ABCD multiplet with centre at 7.04 (4H). Found: C, 55.48; H, 3.17; Mo, 27.70. $C_{16}H_{10}MoO_3$ calcd.: C, 55.50; H, 2.89; Mo, 27.7%.

Preparation of indenemolybdenum tricarbonyl (III)

The experiment was conducted as above. From 0.35 g (3 mmol) of indene, 1.25 g (3 mmol) of $Py_3Mo(CO)_3$ and 1.25 ml (9 mmol) of $Et_2O \cdot BF_3$, 0.16 (18%) of III were obtained, m.p. 125–126°C (dec.) $\nu(CO)(THF)$ 1895, 1976 cm^{-1}. ^1H NMR: AB subspectrum $(H(1)_{exo} + H(1)_{endo})$ δ_A 2.55$(H(1)_{exo})$ δ_B 2.90$(H(1)_{endo})$ J_{AB} 23.5 Hz; coordinated six-membered ring 5.28 (2H), 4.74(2H); olefin protons of five-membered ring 5.94 (H(2) + H(3).

Found: C, 48.47; H, 2.05; Mo, 32.5. $C_{12}H_8O_3Mo$ calcd.: C, 48.6; H, 2.7; Mo, 32.43%.

Preparation of fluorenetungsten tricarbonyl (II)

To 2 g (12 mmol) of fluorene and 2.2 g (4.4 mmol) of $Py_3W(CO)_3$ in 50 ml of dibutyl ether, 3.2 ml (21.6 mmol) of $Et_2O \cdot BF_3$ was added. The mixture was stirred for 2 h at 60–65°C. After being cooled to 25°C, the mixture was diluted with ether

(40 ml) and hydrolysed. The ether layer was passed quickly through $MgSO_4$. After evaporation of the solvent in vacuo, the residue was chromatographed on a silica gel column (3 × 15 cm). Fluorene was washed with petroleum ether and the main yellow zone containing II was eluted with benzene. After reprecipitation twice from benzene/heptane 0.63 g (33%) of II was obtained. M.p. 145–146°C. ν(CO)($CHCl_3$) 1900, 1973 cm^{-1}. ^1H NMR: AB subspectrum ($H(9)_{exo}$ + $H(9)_{endo}$) δ_A 3.05 ($H(9)_{exo}$), δ_B 3.36 ($H(9)_{endo}$), J_{AB} 22 Hz; coordinated six-membered ring 4.46 (H(2) + H(3), 2H), 4.95 (H(1), 1H), 5.32 (H(4), 1H). Non-coordinated six-membered ring: ABCD multiplet with centre at 6.98 (4H). Found: C, 32.96; H, 1.67; W, 32.0. $C_{16}H_{10}O_3W$ calcd.: C, 33.0; H, 1.73; W, 31.83%.

Preparation of bis[tricarbonyl(η^5-fluorenyl)molybdio]mercury (VI)

A hexane solution of BuLi (0.032 g, 0.5 mmol) was added to 0.13 g (0.4 mmol) of I in ether at −70°C. The solution turned red and a red solid was precipitated. The temperature was gradually raised to −10°C and 0.08 g (0.3 mmol) of solid $Hg(CN)_2$ was added. The mixture was then heated slowly to 25°C. The red solid was isolated by decantation and purified by reprecipitation from CH_2Cl_2/CH_3OH. Yield of VI 0.1 g (55%). VI decomposes at 150°C. ν(CO)(CH_2Cl_2) 1905, 1978 and 2002 cm^{-1}. ^1H NMR ($CDCl_3$): singlet at 6.38 (H_9, 1H); multiplet at 7.14–8.38 (8H) (six-membered rings).

Preparation of bis[tricarbonyl(η^5-fluorenyl)tungstenio]mercury (VIII)

A hexane solution of BuLi (0.029 g, 0,45 mmol) was added to 0.15 g (3 mmol) of II in 80 ml of ether at −70°C. The reaction mixture turned red. The temperature was raised to −30°C and stirring was continued for 2 h. Then 0.18 g (0.7 mmol) of solid $Hg(CN)_2$ was added and the mixture was stirred for 1.5 h, the temperature being increased gradually to 25°C. The solvent was removed in vacuo and the residue was extracted with chloroform. After evaporation of $CHCl_3$ the crystals were reprecipitated from benzene/heptane. 0.15 g (40%) of VIII was obtained. VIII decomposes at 131–134°C. ν(CO)($CHCl_3$) 1900, 1980 and 2002 cm^{-1}. ^1H NMR ($CDCl_3$): singlet at 6.33 (H(9) 1H), ABCD multiplet at 7.0–8.1(8H) (six-membered rings). Found: C, 35.37; H, 1.80; W, 34.78, Hg, 17.51. $C_{18}H_{18}HgO_2W_2$ calcd.: C, 36.03; H, 1.88; W, 34.47; W, 18.8%.

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